

**INFRARED ABSORPTION SPECTRUM OF
SOLID DINITROGEN TRIKIDE**

by

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INTRODUCTION AND REVIEW OF LITERATURE

Although the existence of dinitrogen trioxide has long been assumed, very little is known of its properties. Theoretically, dinitrogen trioxide is the anhydride of nitrous acid. It is not very stable and decomposes extensively even at room temperature to give an equimolar mixture of $\text{NO}_2\text{-N}_2\text{O}_4$ and NO. When an equimolar mixture of NO and NO_2 is condensed, a blue liquid which consists of N_2O_3 with undoubtedly some dissolved NO and $\text{NO}_2\text{-N}_2\text{O}_4$ and which boils at about 3.5°C (8) is obtained. The liquid solidifies when temperature is reduced to about -103°C (8). The boiling and freezing points are known only approximately.

The investigation of physical properties of N_2O_3 has been limited by the instability of this oxide. A study of the equilibrium between nitric oxide, nitrogen dioxide and dinitrogen trioxide in the gas phase has been performed by several investigators (1, 2, 13) over a wide concentration range at several temperatures.



Verhoeck and Daniels (13) found that ΔF_{296}° and ΔH° for the reaction were -441 cal. and 10.3 kcal. respectively. The values of the equilibrium constant K_p depended upon the pressure since the gases were not perfect. Reed and Lipscomb (11) obtained the X-ray precession and Weissenberg photographs at -115°C , and found that the unit cell of N_2O_3 containing 32 molecules was tetragonal with $a = 16.4\text{\AA}$ and $c = 8.86\text{\AA}$. They also indicated that a crystal phase transition appeared to occur at about -125°C below which temperature the X-ray patterns suggested a disordered structure. However, they were not able to determine the geometry of this molecule.

The infrared spectrum of NO-NO₂(N₂O₃) in the gas phase has been studied by D'Or and Tarte (3). They found six new bands from the spectra of NO and NO₂ gas mixture. They also suggested the existence of N-N bond in the N₂O₃ molecule from the similarities among the spectra of N₂O₃, N₂O₂ and N₂O₄. Snyder and Hisatsune (12) first obtained the infrared absorption spectra of solid N₂O₃ at -180°C in the course of their study of solid N₂O₄. They reported five absorption bands for solid N₂O₃ and also indicated that the absorption maxima of some bands had a tendency to shift or change their shape on warming the sample, but they did not give the characteristics of the bands or any detailed explanations about the spectrum of N₂O₃.

Two entirely different structures have been proposed for N₂O₃.



(I)



(II)

The structure I has long been accepted as an anhydride of nitrous acid but its configuration was first proposed by Liefer (7) in 1940. The structure II was proposed by Ingold and Ingold (6) in 1947. Liefer showed that if ordinary NO was mixed with NO₂ made from nitrogen rich in N¹⁵, there was a quick exchange of isotopes, evidently through the anhydride, which could decompose in two symmetrical ways:



Furthermore, Pauling (10) suggested that the presence of like formal charges on adjacent atoms such as in structure II made it less stable than the anhydride form I. This suggestion agreed well with the chemical

evidences. Ingold and Ingold, however, have presented arguments which strongly supported the structure II. They pointed out that the unusually long N-N bond distances in N_2O_2 and N_2O_4 molecules in the crystalline state, which had been determined by X-ray studies, might be rationalized in terms of the formal charges on the two adjacent atoms. Recently, extensive work on the infrared spectra of frozen oxides of nitrogen at liquid helium temperature has been performed by Fately, et al. (5). They have proposed an important evidence that, at this temperature, N_2O_3 molecule can exist either as its stable form $ON-NO_2$ (structure II) or as its unstable form $ONONO$ (Structure I) depending on the experimental conditions, and those two species exhibit slightly different absorption patterns.

STATEMENT OF PROBLEM

Although the infrared absorption spectra of simple nitrogen oxides, i.e. nitrous oxide, nitric oxide and nitrogen dioxide, are well known, spectral data on the higher oxides of nitrogen such as dinitrogen trioxide, dinitrogen tetroxide, dinitrogen pentoxide, and nitrogen trioxide (NO_3) are not readily available.

The purpose of the present work was to obtain a reliable infrared absorption spectrum of dinitrogen trioxide in the solid phase in the neighborhood of the reported phase transition temperature of $-125^{\circ}C$ (11) and to observe the phase transition of N_2O_3 by the difference in their infrared absorption spectra.

EXPERIMENTAL

Since dinitrogen trioxide was very unstable, chemically reactive, and had a low boiling point, the study of its infrared absorption spectrum required a high vacuum system, a low temperature apparatus, and special handling techniques.

Apparatus

The Vacuum Line: A glass vacuum line with a two stage, air-cooled, oil diffusion pump (Consolidated Vacuum Corp. Model CF-20a 1292) was used in this work. The diffusion pump, which was filled with Dow Corning No. 704 Silicone fluid, was able to produce a pressure of less than 10^{-6} mm Hg under normal operation conditions. All traps and joints on this line were lubricated with Dow Corning Silicone high vacuum grease which had good mechanical properties and withstood short exposures to nitrogen dioxide. However, extended exposures to this gas destroyed the vacuum seals in the traps and joints. Therefore, traps on storage bulbs for nitrogen dioxide were lubricated with Halocarbon high temperature vacuum grease. This lubricant had a tendency to freeze so that it was not suitable for traps which were used often.

The vacuum line consisted essentially of two sections, one for the preparation and the purification of samples, and the other for the transfer of samples into infrared absorption cells. The preparation line was made similar to that described by Nightingale et al. (9). The transfer line was designed so that samples could be introduced into either a gas cell or low temperature cells. A large mercury column was connected to

the line with a 16/9 ball joint couple so that it could be removed for cleaning. This provision was necessary because the mercury often became contaminated with nitrogen oxides. Small samples of nitrogen oxides of known pressure could be made in the calibrated bulb which was attached to the line between the mercury column and the cell connections. When a large amount of an oxide was required, the preparation was carried out in the preparation line.

The Low Temperature Solid Cell: The cell body was made of Pyrex around a pair of 71/60 standard taper joints. The tubing of the male joint was extended to form the lower cell body as shown in Plate I-A. Short sections of 45 mm o.d. tubing were connected to the lower section, and the edges ground flat for the optical windows. For sample introduction a 4 mm bore high vacuum tap followed by about 6 cm of 25 mm o.d. tubing was sealed perpendicularly to the optical path. A tap of the same bore was connected to the upper part of the cell for evacuation purpose.

The female joint formed the compartment for the refrigerant as shown in Plate I-B. The 14/35 standard taper female joint at the top was for thermocouple outlets. A sturdy, copper-to-glass seal was attached to the lower end of the central tubing. The metal cooling block was then connected to this copper tubing. After the glass cell body was fabricated, the large joints were carefully ground with 600 grade carborundum. This grinding prevented the joints from freezing when liquid nitrogen was introduced into the inner tube.

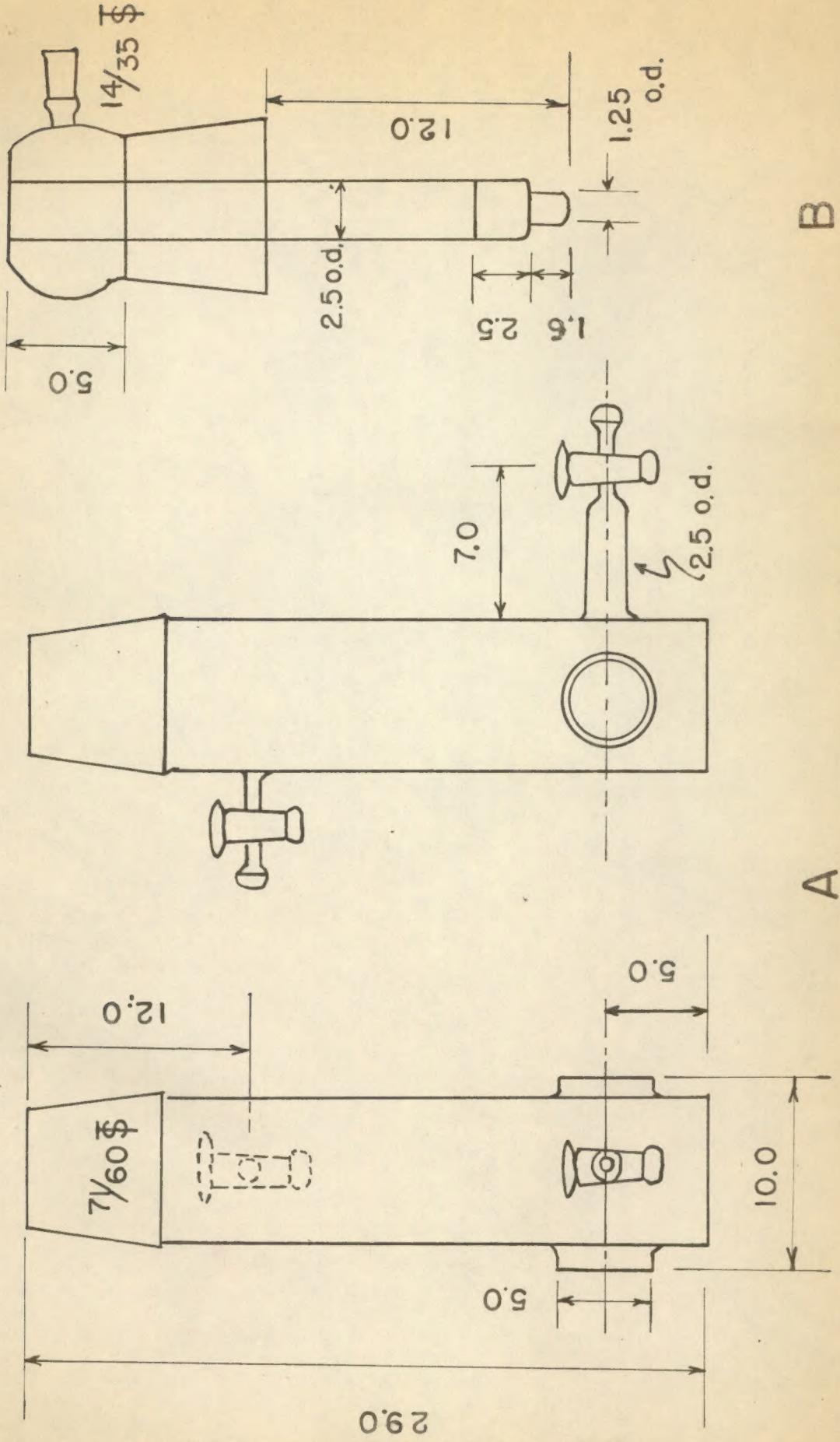
The metal parts for the cooling block are shown in Plate II. A and B were made from a 5 mm thick sheet of either aluminum or copper,

EXPLANATION OF PLATE I

Schematic Diagram of Low Temperature Solid Cell.

- A: Male cell body.
- B: Female cell body and refrigerant compartment.

PLATE I



and C from a 16 mm o.d. copper rod. The connector C was soft-soldered directly to the tip of the copper-to-glass seal. The surfaces on the aluminum plate which were exposed to the nitrogen oxides or which came in contact with sample window were coated with Teflon resin. A thin coating of Du Pont Teflon Primer for steel (No. 850-251) was painted on the surfaces, and baked at about 400°C until the color of the coating changed from brown to blue-green. Three such coatings produced a good, water-proof surface which was inert toward nitrogen dioxide. Similar coatings were attempted on copper surfaces, but these surfaces were too reactive to support a stable coating. The cooling block was assembled by bolting down plate A on B with the sample window between them. The windows were 31 x 30 x 4 mm rectangular plates. KBr outer windows and a silver chloride inner window were used for studying the spectrum from 5500 cm^{-1} to 440 cm^{-1} . When the spectra below 440 cm^{-1} were taken, all optical windows were replaced with cesium bromide.

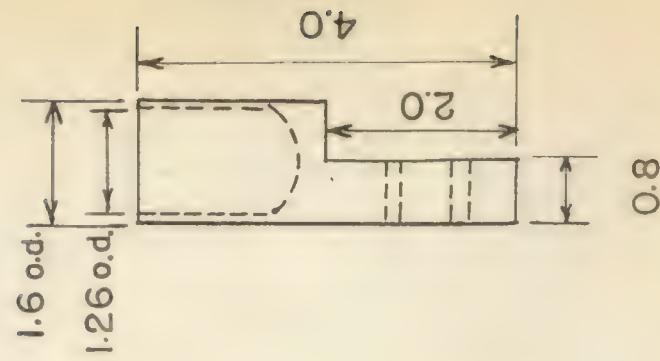
All joints and tops on the cell were lubricated with silicone high vacuum grease. The outer cell windows (50 mm diameter by 5 mm thickness) were attached with Apiezon sealing compound Q. The sealing compound was rolled into a thin, long strip which was then placed around the glass rim. The windows were pressed against the sealing compound and the cell evacuated. These seals were strong enough to hold heavy silver chloride or cesium bromide windows when the cell was opened to the atmosphere.

Temperature Measurements of Sample Window: The temperature of the cooled window was measured with a copper-constantan thermocouple whose junction was imbedded in the middle of the window opposite the surface on which samples were condensed. The junction potentials were read by a

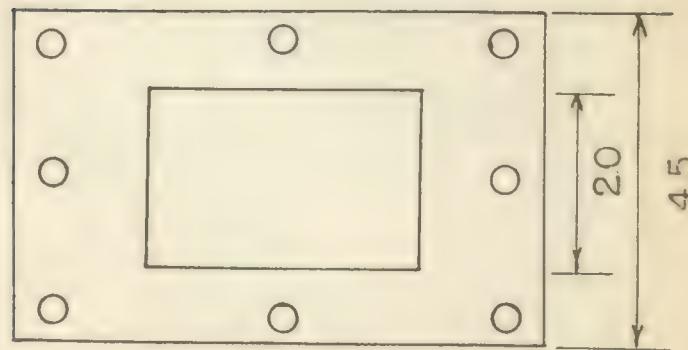
EXPLANATION OF PLATE XI

The Ceiling Block and The Sample Window Holder.

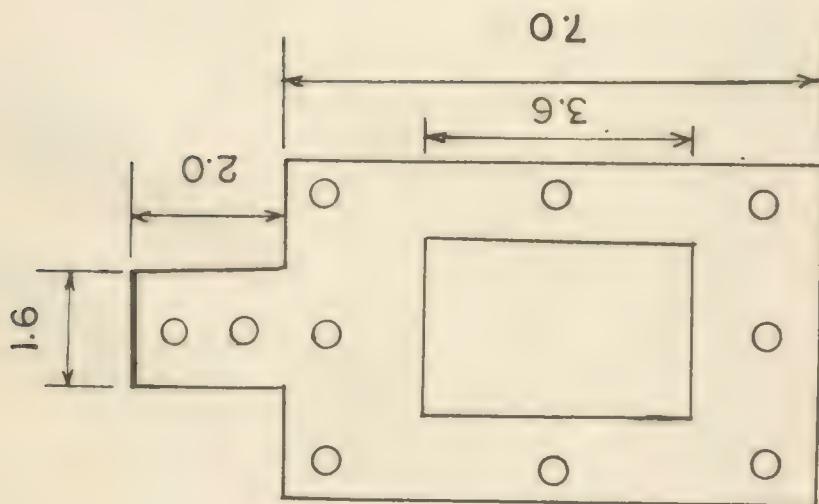
- A and B: Sample window holder made from 5 mm thick
aluminum or copper sheets.
C: The connector made from 16 mm O.d. copper rod.



C



B



A

direct reading potentiometer at five-minute intervals and the potentiometer readings were converted to centigrade temperature according to "HANDBOOK OF CHEMISTRY AND PHYSICS" 38th edition. Since the Teflon coating formed a good thermal insulation, the lowest temperature attained in this work was about -160°C with the aluminum plates in the cell under normal operation conditions with liquid nitrogen refrigerant, and about -170°C with the copper plates in the cell with the same refrigerant.

Infrared Spectrometer: Infrared absorption spectra of solid dinitrogen trioxide and diazotrogen tetroxide were obtained with two infrared spectrometers. A Perkin-Elmer 137, double beam Infracord spectrometer with a sodium chloride prism was used in preliminary runs and in checking the concentrations. A Perkin-Elmer 112 single beam, double pass spectrometer with lithium fluoride, sodium chloride, potassium bromide and calcium bromide prisms was used to record the spectra from 2.4 to 35 μ . These prisms were calibrated according to Bunnis et al. (4). The spectra were reproducible to within the limits shown in Table 1.

Table 1. Spectral reproducibility

Region	4000 cm ⁻¹	3000 cm ⁻¹	2000 cm ⁻¹	1000 cm ⁻¹	Below 1000 cm ⁻¹
Accuracy	± 20 cm ⁻¹	± 10 cm ⁻¹	± 5 cm ⁻¹	± 3 cm ⁻¹	± 1 cm ⁻¹

In order to eliminate the pronounced background absorption of atmospheric water and carbon dioxide, dried air was passed into the spectrometer housing and the cell compartment. The drying column consisted of four 112 mm by 3.5 mm o.d. glass columns which were connected in series and were filled with alumina. Columns were reactivated by electrical heating after every twenty-hour period.

Chemicals

Nathanson Company nitrogen oxides were used in this work. Both nitric oxide and nitrogen dioxide contained considerable amount of impurities, i.e. free nitrogen, nitrous oxide, dinitrogen trioxide, nitrogen dioxide (or nitric oxide) and most likely nitric acid, so that the gases had to be carefully purified.

Nitric Oxide: Nitric oxide was purified by distillation in a manner somewhat similar to that described by Nightingale et al. (9). Nitric oxide from Nathanson Company lecture bottle was passed through a trap immersed in a dry ice-acetone bath, which removed higher boiling impurities, and condensed further down the vacuum line with liquid nitrogen. This sample was distilled several times until the infrared spectrum showed only the absorption bands due to nitric oxide. The most difficult impurity to remove from the sample was nitrous oxide as Nightingale indicated. Although Nightingale indicated that there was no convenient way of separating N_2O from nitric oxide completely, it was found that nitrous oxide can be removed effectively by using a trap cooled with an ethyl bromide slush, which had a temperature of about $-110^{\circ}C$, between the dry ice-acetone and the liquid nitrogen traps on the vacuum line. Several distillations were carried out through this series of traps. A trace of nitrous oxide was easily detected by the strong absorption band at 3140 cm^{-1} in the infrared spectrum of the sample. The purified nitric oxide condensed to give a blue liquid which froze to a light blue grey solid. The gaseous nitric oxide was colorless.

Nitrogen Dioxide-Dinitrogen Tetraoxide Equilibrium Mixture:

$\text{NO}_2\text{-N}_2\text{O}_4$ equilibrium mixture was purified by condensing the Matheson tank gas with dry ice-acetone bath and pumping out the uncondensable gases. The gas which condensed in dry ice-acetone trap was passed through a P_2O_5 drying column several times. Then, purified oxygen was added to this sample in order to oxidize the dinitrogen trioxide impurity. The excess oxygen was then pumped off while the sample was frozen out with a dry ice-acetone bath. The sample was white crystalline solid when condensed with dry ice-acetone bath or with liquid nitrogen.

Dinitrogen Trioxide: Dinitrogen trioxide decomposes rapidly and extensively at room temperature and consists, essentially, of a mixture of NO and $\text{NO}_2\text{-N}_2\text{O}_4$ with a small equilibrium concentration of N_2O_3 . Therefore, the following two gas mixtures were examined throughout this work.

1. A stoichiometric mixture of nitric oxide and oxygen: Since the pressure of these gases could be measured separately with an ordinary mercury manometer, a known quantity of purified nitric oxide was mixed with one-fourth as much of purified oxygen. A sufficient time had to be allowed for the reaction to go to completion because this oxidation was slow.

2. A mixture of NO_2 with an excess of NO : Since NO_2 not only attacked mercury but also existed as an equilibrium mixture with N_2O_4 at ordinary temperatures, the exact concentration of NO_2 was not determined. Therefore, an excess of purified NO was added to the purified $\text{NO}_2\text{-N}_2\text{O}_4$, and allowed to react.

The former method had the advantage of allowing one to estimate the approximate concentration of the sample on the window. However, the spectra always showed higher concentration of N_2O_3 . On the other hand, the latter method gave spectra showing relatively high concentrations of N_2O_3 .

General Procedure

The cell was first evacuated until the pressure was below 10^{-6} mm Hg, and then liquid nitrogen was introduced into the refrigerant compartment. After the cold window had attained equilibrium, samples of nitrogen oxides were introduced from a calibrated volume tubing attached to the lower 18/9 ball joint on the cell jacket. Polycrystalline film of samples was condensed onto the silver chloride or cesium bromide window of the cell by means of either sublimation from the solid or a series of "shots" of the vapor. The large female joint was then rotated until the plate was perpendicular to the optical path. Since these joints had been carefully ground, it was possible to rotate them with liquid nitrogen in the cell, even after more than a week of continuous use without regreasing.

As the equilibrium studies indicated, if the N_2O_3 molecule was stable or, at least, its dissociation constant became small at lower temperatures, there should be a difference between the two methods of sample condensation. One might expect that the sublimation method would give pure N_2O_3 whereas the expansion method would result in a mixture of N_2O_3 and N_2O_4 . But the differences between these two methods of condensation were not apparent from their spectra. In both cases the spectra were those resulting from a mixture of N_2O_3 and N_2O_4 solids. However, when a small amount of sample containing an excess of nitric oxide was condensed, a relatively purer N_2O_3 spectrum was obtained. Therefore, it was apparent that the N_2O_3 molecules were dissociated into nitric oxide and nitrogen dioxide in the gas phase regardless of the initial states of the samples, and that the solid N_2O_3 was deposited onto the window through collision between nitric oxide and nitrogen dioxide molecules at the window surface.

When a mixture of N_2O_3 and N_2O_4 was condensed on the cooled windows, the film formed was, in general, foggy at first and changed to a bluish white film as the concentration increased. If a sample as deposited was warmed slowly, its appearance remained unchanged until the temperature reached about $-100^{\circ}C$, at which temperature the blue color disappeared and the film became crystalline white. With further warming, sublimation from the window occurred at about $-40^{\circ}C$. However, when pure N_2O_3 was deposited, the window appeared as clear transparent blue plate. No fogging appeared until the temperature reached about $-100^{\circ}C$ at which point the film became crystalline white. Such behavior confirmed that N_2O_3 molecules could exist as stable solid at below $-100^{\circ}C$ and above the temperature it decomposed rapidly into NO and NO_2 . The nitric oxide then sublimed from the cold window to the metal block leaving NO_2 which dimerized rapidly into N_2O_4 on the window.

The windows used on the solid cell, except silver chloride, were attacked by the samples and nitrates were formed. Since the absorption bands of the nitrate ion, especially the 7.4μ band, overlapped with the bands of the sample, whenever the blank spectrum showed nitrate bands, the windows were repolished until the nitrate bands completely disappeared. It was found that the oxides of nitrogen do not react with these windows so long as the temperature of the windows were below about $-110^{\circ}C$. However, when the cell was warmed to remove the sample, considerable reaction occurred at the surface.

INFRARED ABSORPTION SPECTRAThe Spectrum of Solid Dinitrogen Tetraoxide

The spectrum of pure N_2O_3 in the solid state could not be obtained in this work since its spectra always consisted of those resulting from N_2O_3 and N_2O_4 . Therefore, it was necessary to obtain the spectrum of N_2O_4 first in order to identify the spectrum of N_2O_3 .

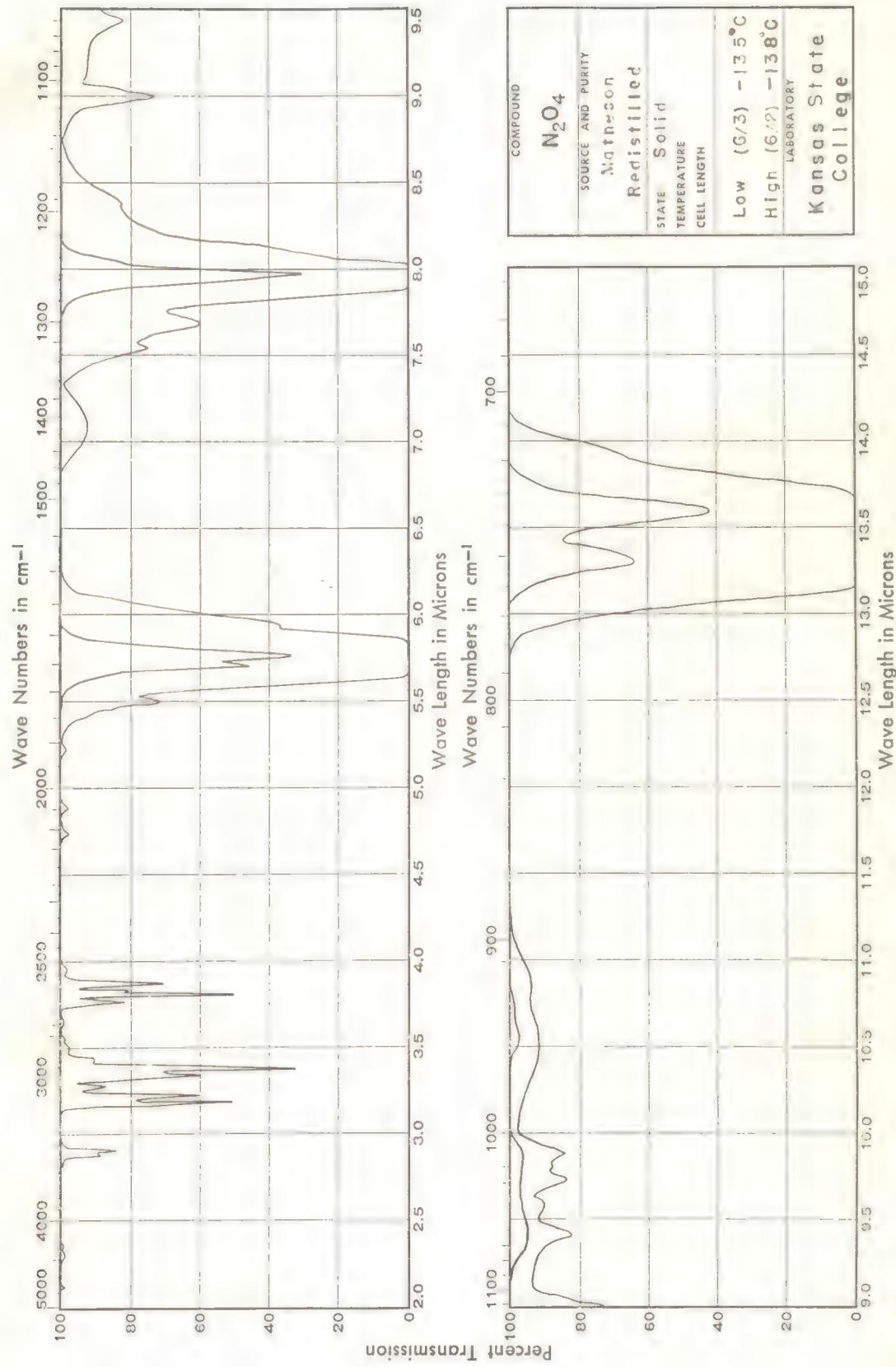
Although the infrared spectra of N_2O_4 in solid phase at -180°C have been reported by Snyder and Nicotra (13) and by Wiener and Nixon (14), there were differences between the reported frequency values of overtones and combination bands as well as of fundamental bands. Thus these data could not be used directly for the identification of N_2O_3 bands in this work. Therefore, the spectra of N_2O_4 were taken under identical experimental conditions as those used for N_2O_3 . The observed absorption spectrum of solid N_2O_4 is shown in Plate III A and III B, and the absorption maxima are listed in Table 2. Previously published frequency values are also given for comparison. When the strong bands at 3.39 μ , 6.24 μ , 7.69 μ and 12.80 μ showed total absorption on the "infrared" spectrum, that run was arbitrarily called a "high concentration" run. Other runs were called "lower concentration" runs. If the temperature of the cold window was below -110°C, the run was called as a "lower temperature" run and above this temperature a "higher temperature" run.

EXPLANATION OF PLATE III A AND III B

The Infrared Absorption Spectrum of Dinitrogen Tetraoxide
from $2\text{ }\mu$ to $35\text{ }\mu$.

Concentration	Spectral range	Spectral number	Temperature during sample condensation	Final temperature
High	$2.0\text{ }\mu$ - $16.5\text{ }\mu$	58-6-02	-126°C	-130°C
Low	$2.0\text{ }\mu$ - $14.5\text{ }\mu$	58-6-03	-135°C	-130°C
High	$14.5\text{ }\mu$ - $35.0\text{ }\mu$	58-7-29	-115°C	-101°C
Low	$14.5\text{ }\mu$ - $35.0\text{ }\mu$	58-8-11	-112°C	-110°C

PLATE III A



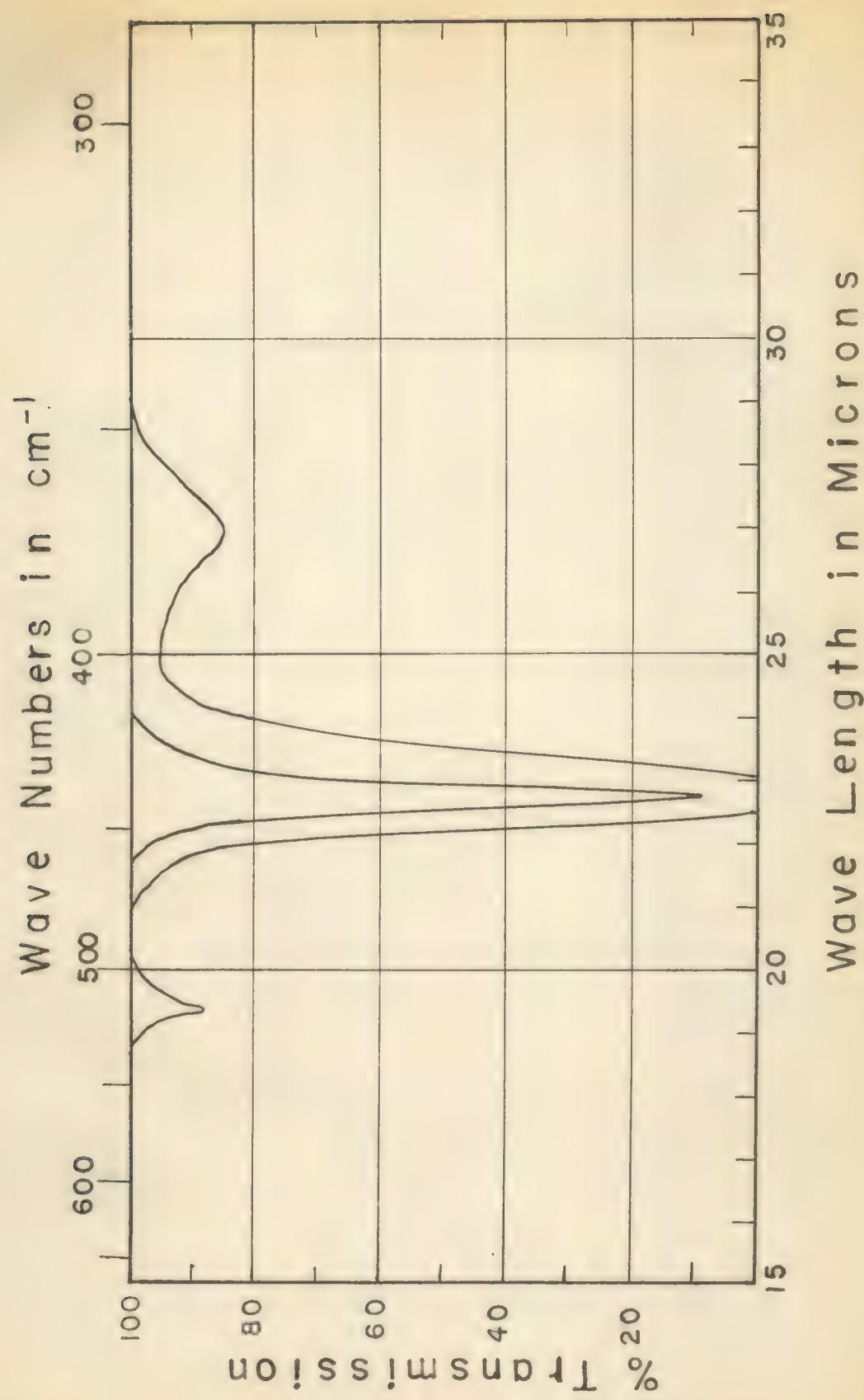


Table 2. The observed infrared spectrum of solid dinitrogen tetroxide (cm^{-1})

This Work -110°C	Relative Intensity	S.M. (a) -180°C	W.N. (b) -180°C	F.R.C. (c) No b.p.
~3200	vw	~3200 ~5000	vw	
4000	vw			
4334?	vw	4320 ~4270	vw vw	
4226?	vw	~4190?		
{ 3467	w			3460 w
3428	w	3424	w	3430 w
{ 3134	w	{ 3133	w	3136 m
3115	w			
3059	w	{ 3103	w	3105 m
{ 3054 sh	v	{ 3079	w	3080 vw
3031	v	{ 3056	w	3058 vw
{ 2990	w			2986 w
2948	w	2957	m	2958 m
2925	vw			
~2862 B	vvw			
2820?	vvw			
2698	v			2635 w
{ 2636	m	2631	w	2626 s
2612	w			
2582	vw	2590	w	2584 w
2586	vvw	~2542?		
2103?	vvw			
2046?	vvw			
1950?	vvw	1964	w	
{ ~1833	w			1839 w
{ 1768 sh	v			1829*
1752	s	1749	s	1760 vs
1738	s	1728	s	1734 vs
1685?	w	1680 1581	w w	(1690) 1645*
~1410 B	vw	~1400 B	w	(1371)
{ 1325 sh	w			(1364)
1300	w			1280 m
1254	s	1255	s	1256 vs
{ 1236 sh	vw			1262
~1100	vw			1262
1110	v	1119	vw	
{ 1061	w			
1042 B	w			
1026	w			
1011	w			
~950 B	w			
		815	vw	

Table 2. (Concl.)

This Work -130°C	:	Relative Intensity	:	S.R. (a) -130°C	:	W.W. (b) -130°C	:	P.B.C. He b.p.
752	:	s	:	754	s	756	vs	787*
737	:	s	:	737	s	738	vs	755
				~678	vw			752
~512		vw		512?				740
449		s		442	s	441	m	
372		w		346	m			
						(163)		
				(49)		(18-30)		

Keys: s - strong, m - medium, w - weak, v - very, b - broad, sh - shoulder
() - calculated value, ? - uncertain band, * - CHONO_2 band.

- (a) Snyder and Rissetzke: (12)
- (b) Wiener and Nixon: (14)
- (c) Tateley, Bent and Crawford: (5)

The Spectrum of Dinitrogen Trioxide

Dinitrogen trioxide was studied in thirty separate runs, one half of the runs with thin films and the other half with thicker films at various temperatures. With every sample, at least, two spectra were taken successively. A spectrum of $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$ solid mixture, which was taken at about -135°C is shown on Plate IV A and IV B.

The absorption bands, which were assigned to the species N_2O_3 , were obtained by comparing the spectrum of $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$ solid mixture with that of pure N_2O_3 . The possibility of the presence of NO in the $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$ sample was immediately ruled out by observing the fact that NO has an appreciable vapor pressure even at liquid nitrogen temperature so that it could not be kept on the window. It was possible to condense some NO on the cold window of the low temperature solid cell, but it soon sublimed to the upper

EXPLANATION OF PLATE IV A AND IV B

The Infrared Absorption Spectrum of Dimethylenetrifluoroacetone
from 2 μ to 35 μ .

Concentration	Spectral range	Spectrum number	Temperature during sample preparation	Final temperature
High	2.0 μ -14.5 μ	58-3-26	-164°C	-112°C
Low	2.0 μ -14.5 μ	58-4-11	-162°C	-135°C
High	14.5 μ -35.0 μ	58-8-06	-162°C	-112°C
Low	14.5 μ -35.0 μ	58-7-21	-162°C	-135°C
320 cm^{-1} band				

PLATE IV A

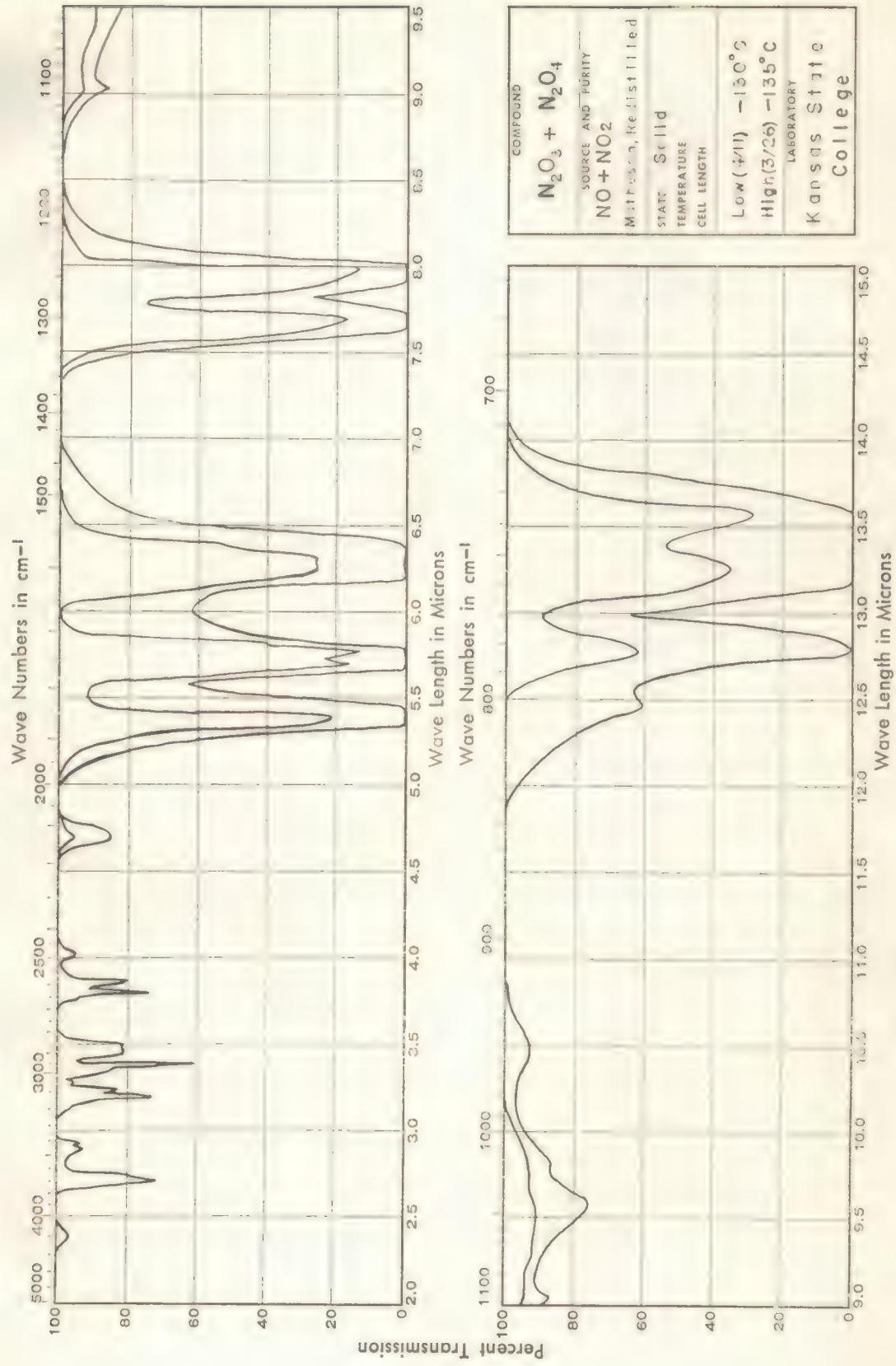
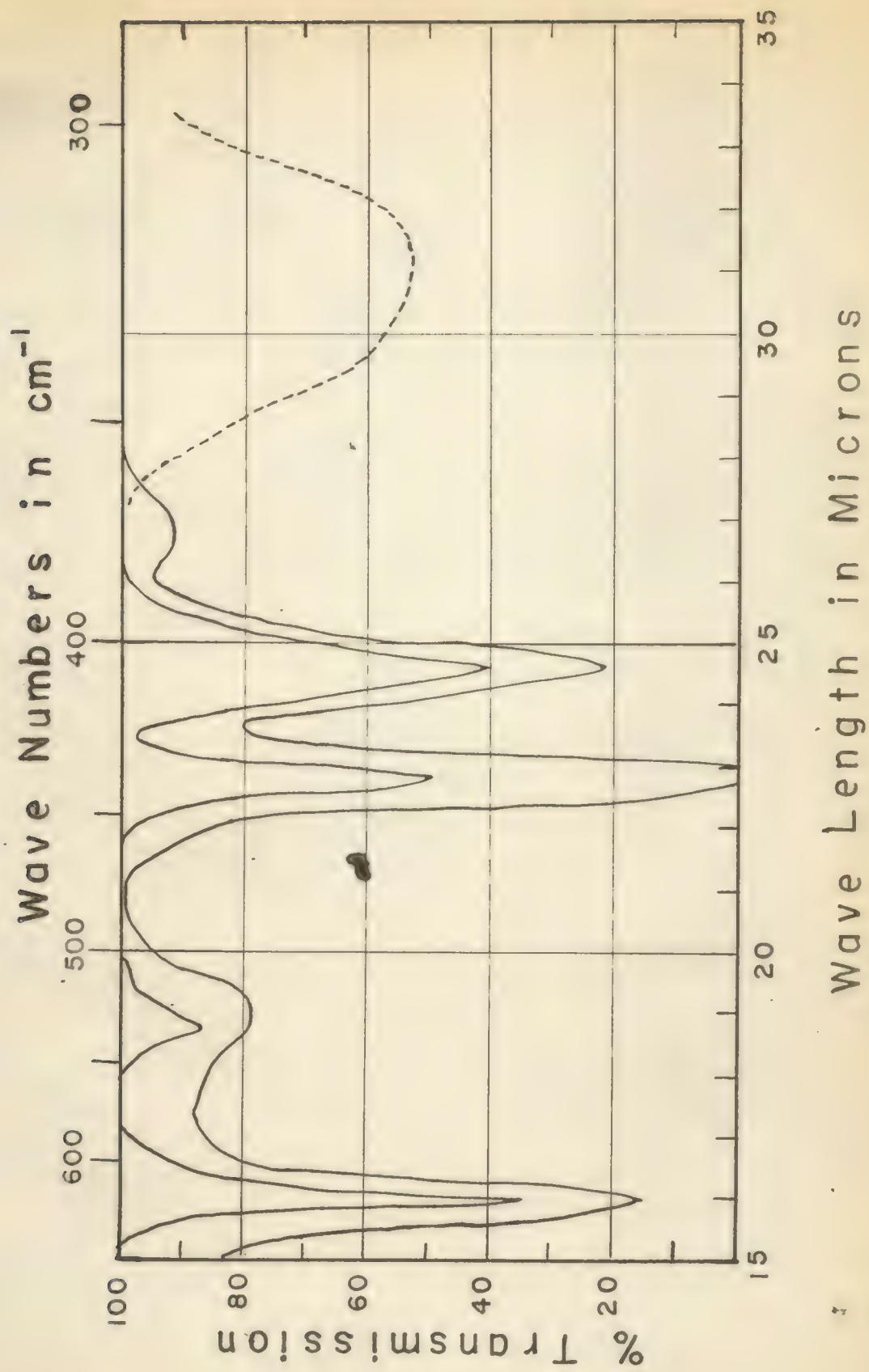


PLATE IV B



glass section which was in direct contact with liquid nitrogen. Since it was found that Dow Corning high vacuum grease dissolved in the oxides of nitrogen and its absorptions appeared on the spectra, careful attention was paid to eliminate these absorptions from the spectra of the sample. The broad band ranging from 9μ to 11μ on Plates III A and IV A which overlaps with the sample absorptions was identified as a band due to grease.

Nineteen bands were identified as N_2O_3 absorption bands from the spectra of solid $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$. The appearances and the characteristics of these bands were as follows.

Lithium Fluoride Prism Region

The 3706 cm^{-1} band: A medium intense absorption band appeared just at the region of the 2.7μ water band. In lower concentration runs, the band shape was masked by the atmospheric water absorption. However, in higher concentration runs, this band appeared as a symmetrical and sharp band with moderate intensity.

The 3176 cm^{-1} band: Since this weak band overlapped with a fairly strong N_2O_4 band at 3134 cm^{-1} , careful attention had to be paid in its identification. This band was well separated from the 3134 cm^{-1} N_2O_3 band provided the concentration of N_2O_3 was much higher than the concentration of N_2O_4 . In some runs the band appeared as a shoulder on the 3134 cm^{-1} band or was hidden completely depending on the relative concentration of N_2O_3 to N_2O_4 .

The 2889 cm⁻¹ and 2861 cm⁻¹ Bands: These bands were readily assigned to N_2O_3 because they were well separated from the N_2O_4 bands except that the higher frequency wing of the 2889 cm^{-1} band overlapped slightly with a very weak N_2O_4 band at 2925 cm^{-1} . These two bands showed interesting band contour changes when the temperature was varied as shown in Plate V. In lower temperature runs, the two bands had approximately the same intensities and appeared as a single broad band with a slight dip on the peak. In higher temperature runs, the intensity of the 2889 cm^{-1} band was greatly decreased and the absorption peak was shifted to high frequency. The separation between these two bands was approximately 27 cm^{-1} in low temperature runs and about 40 cm^{-1} in high temperature runs respectively. The 2889 cm^{-1} band disappeared completely in a spectrum taken at about -100°C. Neither the intensity change nor the frequency shift of the 2861 cm^{-1} band was observed.

The 2363 cm⁻¹ Band: This was a weak band and very close to the 2382 cm^{-1} N_2O_4 band so that it could not be resolved well. However, when the concentration dependence of the band was carefully studied and compared with pure N_2O_4 spectra, it became apparent that this band resulted from both N_2O_3 and N_2O_4 absorption.

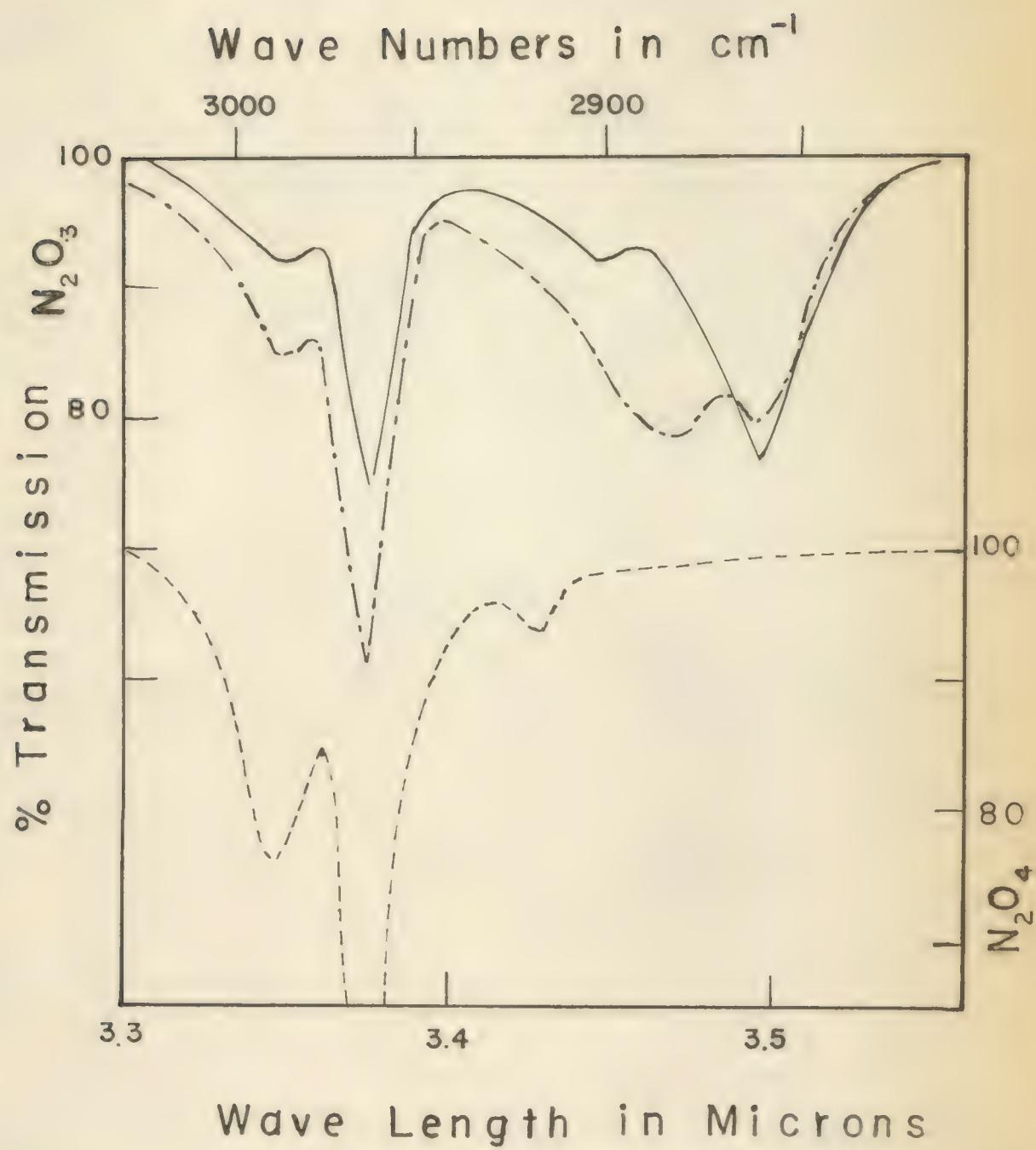
The 2499 cm⁻¹ Band: This was a very weak and broad band. Since no absorption occurred in this region on the N_2O_4 spectra, it was readily assigned to N_2O_3 . The absorption peak of the band could be reproduced to within two wave numbers.

EXPLANATION OF PLATE V

The Spectra of the 2861 cm^{-1} Band Region.

Sample		Spectrum No.	Temperature during sample condensation	Final temperature
solid line	$\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$	56-5-30	-122°C	-100°C
dash-dot line	$\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$	58-5-36	-144°C	-138°C
dashed line	N_2O_4	58-6-05	-140°C	-124°C

PLATE 1



Sodium Chloride Prism Region

The 2126 cm^{-1} Band: A weak band was observed at about 2126 cm^{-1} on the spectra of $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$ mixture. The band showed significant frequency shifts as the temperature changed. The average absorption maximum of the band in lower temperature runs was 2126 cm^{-1} but it shifted about 12 cm^{-1} to the high frequency side in the higher temperature runs.

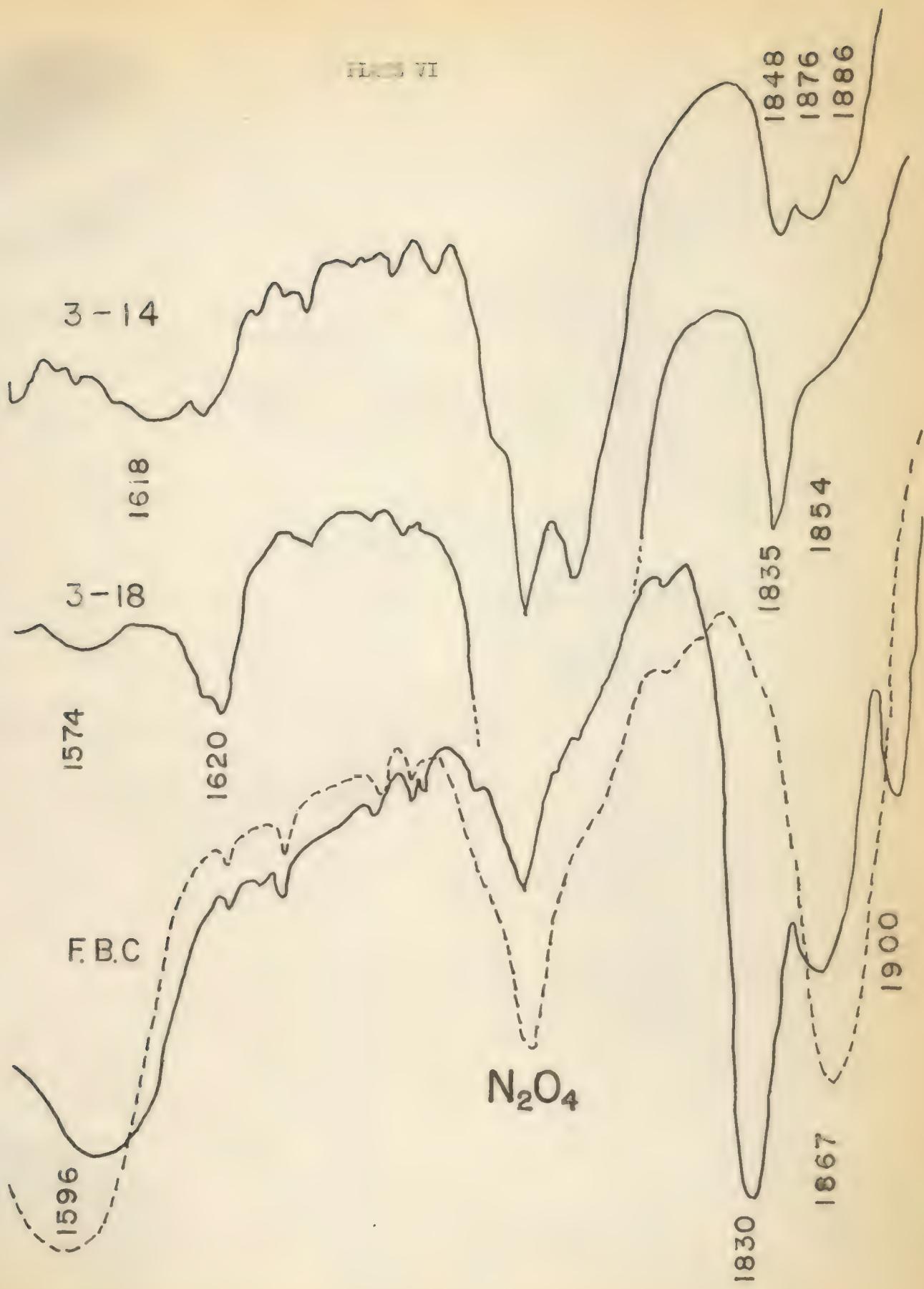
The 1857 cm^{-1} Band: The band at 1857 cm^{-1} was one of the strongest N_2O_3 absorption band. This band could be readily assigned to the nitric oxide group stretching fundamental band. In most runs, the band appeared as a single sharp band whose peak was slightly displaced to the low frequency side of the band center as shown in Plate VII. In few runs, unusual absorption bands were obtained as shown in Plate VI. The spectrum 3-14 and 3-18 were actually obtained in this work while the spectrum F.B.C. was taken from the unpublished work of Fataley, et al. (5) of the University of Minnesota. In the spectrum 3-14, which was taken at about -110°C after the sample was condensed at -125°C , the band was split into three separate branches at 1886 cm^{-1} , 1876 cm^{-1} and 1848 cm^{-1} . In the spectrum 3-18, which was also taken at about -110°C after the sample was condensed at -140°C , the band peak shifted about 22 cm^{-1} to the lower frequency side and only a shoulder appeared at the original position. This splitting of the band was not regularly reproduced and this peculiar behavior occurred only in high temperature runs. The Spectrum F.B.C. in the same plate was observed by Fataley et al. at liquid helium temperature. They also observed that the bands at 1900 cm^{-1} and 1830 cm^{-1} disappeared

EXPLANATION OF PLATE VI

The Appearances of the 1857 cm^{-1} and 1602 cm^{-1} Bands.

Sample	Spectrum No.	Temperature during sample condensation	Final temperature
3-14 $\text{N}_2\text{O}_3-\text{N}_2\text{O}_4$	58-3-14	-128°C	-110°C
3-18 $\text{N}_2\text{O}_3-\text{N}_2\text{O}_4$	58-3-18	-140°C	-110°C
P.B.C. NO-NO_2	Solid line	-268°C	-268°C
P.B.C. NO-NO_2	Dotted line	-268°C	Warmup

PLATE VI



EXPLANATION OF PLATE VII

The Spectrum in the 1720 cm^{-1} band region.

Sample: $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$

Spectrum number: 38-3-10

Temperature during sample crystallization: -13°C

Final temperature: -130°C

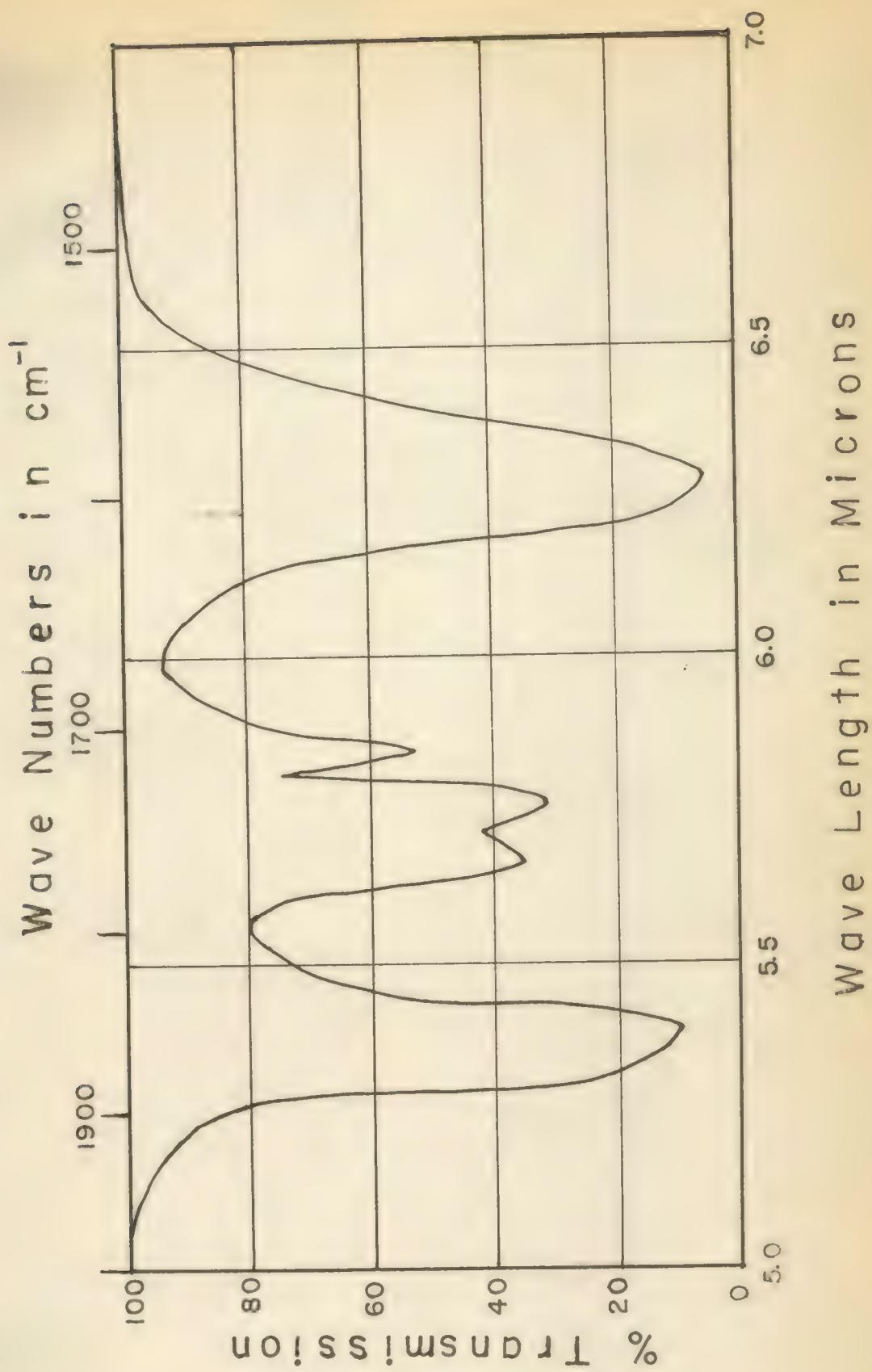


PLATE VII

completely upon warming as shown by the dotted line. Furthermore, they suggested that these two bands may belong to the unstable molecule ONONO . According to their suggestion, since the higher the temperature, the less stable the molecule ONONO , these splitting should be observed more frequently in the lower temperature runs than in the higher temperature runs. However, our result indicated otherwise.

The 1720 cm^{-1} Band: The medium intense band at 1720 cm^{-1} was observed in a rather difficult region to be identified because it was not only close to the strong 1752 cm^{-1} band of N_2O_4 but also overlapped with the background absorption due to atmospheric water. In most spectra, it appeared as a shoulder of the 1752 cm^{-1} band and sometimes hidden completely by this N_2O_4 band. However, a sharp and well separated band was obtained when the concentration of N_2O_4 was greatly reduced and a moderate concentration of N_2O_3 was maintained as shown in Plate VII. The band disappeared completely when the window was warmed from about -135°C to about -115°C and recooled to the original temperature.

The 1619 cm^{-1} and 1602 cm^{-1} Bands: A sharp, strong band was observed at 1602 cm^{-1} . This band could be assigned to the nitrogen dioxide group antisymmetric stretching mode. In most of low temperature runs, the band usually appeared as a single band with the absorption maximum at 1602 cm^{-1} . In higher temperature runs, however, the band was split into two distinct bands with maxima at 1619 cm^{-1} and 1579 cm^{-1} . The band contour was very sensitive to temperature changes. In Plate VI, four different spectra which were taken at different temperatures are shown. Since concentrations were not the same, a quantitative comparison could not be

weak, but the overall temperature dependence of the band was apparent. At liquid helium temperature, this band shifted about 13 cm^{-1} to low frequency side according to the report of Tateley et al. (5).

The 1366 cm^{-1} Band: A sharp, symmetrical, and intense band appeared at 1366 cm^{-1} . This band could be assigned to the nitrogen dioxide group symmetric stretching fundamental band. Although its band contour was very sensitive to temperature changes, it appeared always as a single band throughout this experiment. However, in a single run of thirty runs, the band contour was split into two branches with the separation of about 23 cm^{-1} . In this run, the sample was condensed at about -152°C and the spectrum was taken at about -139°C . The spectrum showed nearly pure N_2O_3 .

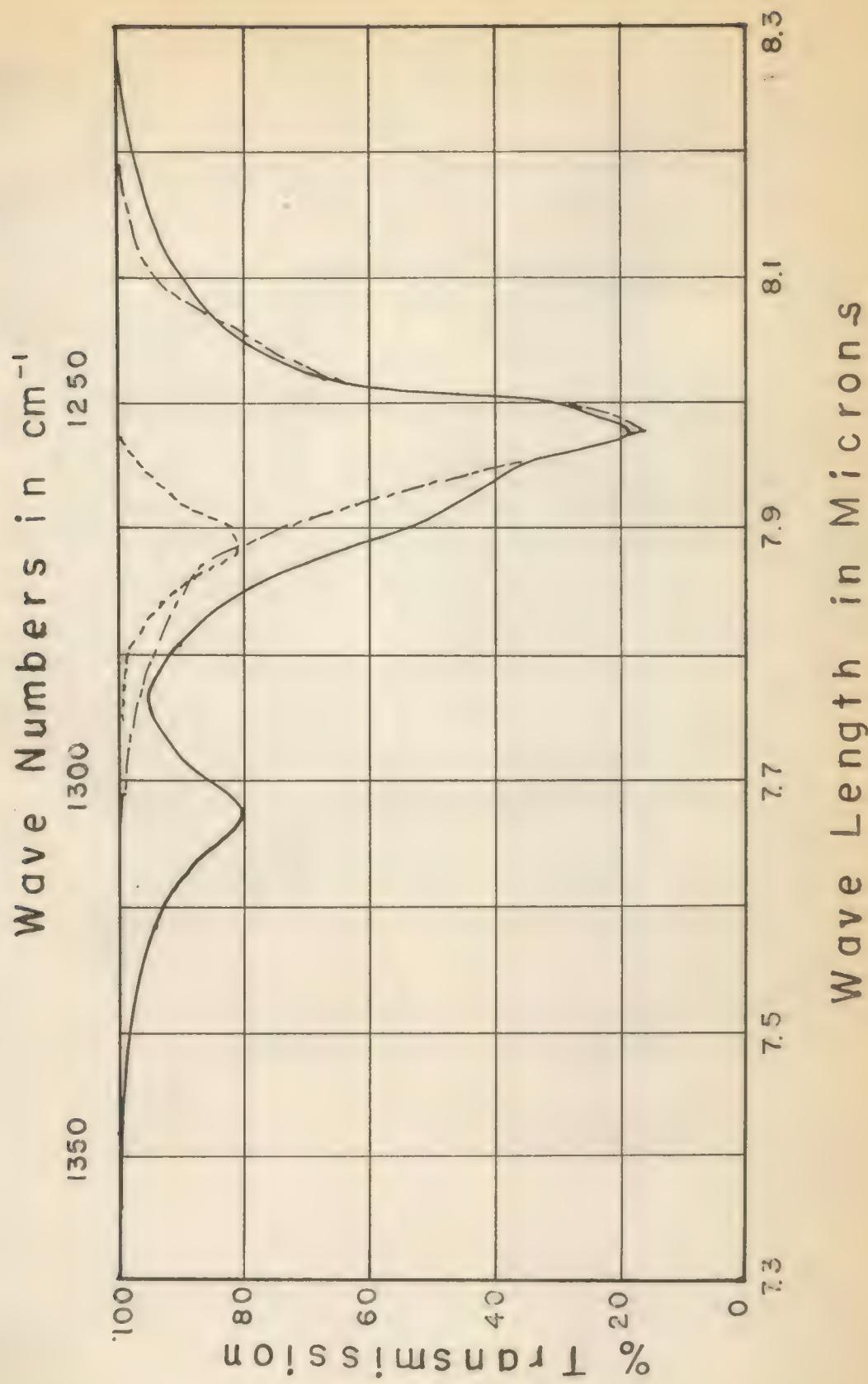
The 1254 cm^{-1} Band: In most spectra, this band was completely hidden by the intense 1234 cm^{-1} N_2O_4 band. It could not be detected even when the spectra showed much higher concentration of N_2O_3 than N_2O_4 . When the shape of the 1254 cm^{-1} band of pure N_2O_3 spectrum was carefully compared with approximately the same concentration of $\text{N}_2\text{O}_3\text{-N}_2\text{O}_4$ spectrum, a definite but weak N_2O_3 band was observed. In Plate VIII, the appearance of the band is shown. However, in some of relatively pure N_2O_3 spectra, the 1234 cm^{-1} N_2O_4 band had appeared as a very sharp, single and perfectly symmetric band so that no overlapping or hidden band was likely to be present. Therefore, this band might be a band which was sensitive to temperature or due to an impurity.

The 1044 cm^{-1} Band: A medium intense band was observed at 1044 cm^{-1} . The band overlapped extensively with four weak bands of N_2O_4 (1061 cm^{-1} , 1043 cm^{-1} , 1026 cm^{-1} and 1011 cm^{-1}) and two bands due to Dow Corning

The Appearance of the 1260 cm^{-1} Band.			
Sample No.	Temperature during sample annealing	Temperature during final annealing	Final
58-4-10	-115°C	-115°C	-115°C
58-5-96	-115°C	-115°C	-115°C
58-6-96	-115°C	-115°C	-115°C
58-7-96	-115°C	-115°C	-115°C
58-8-96	-115°C	-115°C	-115°C
58-9-96	-115°C	-115°C	-115°C
58-10-96	-115°C	-115°C	-115°C

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PLATE VIII



high vacuum grease (1125 cm^{-1} and 1073 cm^{-1}). The impurity band had appeared as a very broad band ranging from 1150 cm^{-1} to 950 cm^{-1} . The shape and the intensity of the 1044 cm^{-1} band was markedly changed depending on the concentration of N_2O_4 and the impurity.

The 802 cm^{-1} Band: In most runs, this band appeared as a shoulder on the 782 cm^{-1} N_2O_3 band. However, when the spectrum showed relatively pure N_2O_3 , its absorption maximum was separated from the 782 cm^{-1} band. The appearance of the band was greatly affected by several factors such as the concentration ratio of N_2O_3 to N_2O_4 , the method of sample condensation and the temperature of the window.

The 782 cm^{-1} Band: A sharp, strong band was observed at 782 cm^{-1} . This band was always accompanied by a fairly strong shoulder on the high frequency side at about 802 cm^{-1} and followed by a very intense N_2O_4 band at 732 cm^{-1} . This band was the only strong band which did not exhibit the band contour splitting in high temperature runs. It could be assigned to the nitrogen dioxide group deformation mode.

Potassium Bromide Prism Region

A medium intense absorption band was observed at 625 cm^{-1} . Since the spectrum of pure N_2O_4 showed no absorption in this region, it was assigned to N_2O_3 . The band was independent of temperature changes and could always be reproduced within one wave number.

Cesium Bromide Prism Region

The 332 cm^{-1} band: A weak band was observed at about 332 cm^{-1} . This band was not only near the 312 cm^{-1} N_2O_3 band but the absorption was further complicated by the pronounced background absorption due to atmospheric water. The band had nearly the same intensity as the 312 cm^{-1} N_2O_3 band, and both bands appeared as a single broad band in some spectra.

The 406 cm^{-1} band: A medium intense band was observed at 406 cm^{-1} which was the region of nitrogen dioxide group wagging vibration. Although the band was broad and overlapped with the strong N_2O_3 band at 440 cm^{-1} and with the atmospheric water bands, it could be observed with an accuracy of one wave number. However, in one run, the band maximum was shifted about six wave numbers to the high frequency.

The 310 cm^{-1} band: A very broad, medium intense band which had the absorption maximum at about 310 cm^{-1} was observed only once on the spectrum which was taken at about -113°C after the sample was condensed at about -138°C . This band was shown in dotted line on Plate IV B. It was interesting to note that this band and the shifting of 406 cm^{-1} were observed on the same spectrum.

SUMMARY

The infrared absorption spectrum of solid N_2O_3 from 2μ to 35μ are shown in Plate IV A and IV B. The frequencies of the observed absorption maxima at two different temperatures are given in the first and second columns of Table 3. In the third column, the relative intensities as well as the overall band shapes are indicated.

Previous data on solid N_2O_3 at $-180^{\circ}C$ by Snyder and Misato, at $-263^{\circ}C$ by Pataley et al. and gaseous N_2O_3 at room temperature by D'Or and Tarte are listed for comparison.

In this work, the quantitative study of temperature dependence of the spectra or the intensity changes of each absorption band due to concentration changes could not be made, but an overall effect of these changes was deduced from a large number of spectra which were taken at various experimental conditions.

The spectra of solid N_2O_3 always showed four intense bands presumably fundamentals, at 1837 cm^{-1} , 1602 cm^{-1} , 1300 cm^{-1} and 782 cm^{-1} . These bands can be assigned readily as the nitric oxide group stretching, the anti-symmetric stretching in the dioxide group, the symmetric stretching in the lone group and the nitrogen dioxide group deformation, respectively. The assignment of the remaining bands must wait further experimental work and theoretical consideration.

The relative intensities of the bands depend quite markedly on such factors as the concentration ratio of N_2O_3 to N_2O_4 , the temperature of the window during the deposition of the sample, the method of sample condensation, and the subsequent temperature of the sample during warmup. The spectrum showed significant differences depending on the temperature. There was a general tendency for most N_2O_3 absorptions to sharpen when the temperature was above $-110^{\circ}C$ compared to that at $-130^{\circ}C$. Certain absorptions (2000 , 1720 , and 902 cm^{-1}) showed characteristic contour changes such as disappearing or weakening upon warming. Other absorptions (1806 , 1648 , and 320 cm^{-1}) which did not exist at one temperature appeared as fairly strong bands at another temperature.

Table 3. The absorption maxima of dinitrogen trioxide.

Observed Low temp., 3706 (cm ⁻¹)	High temp., 3710 (cm ⁻¹)	Intensity: m	: S.M. (a) -180°C	F.R.C. (b) No b.p.	B.T. (c) Room temp.
3176	3175	vw			
{ 2889	{ 2902	v			
2861	2865	v			
2585		vw			
~2490	~2492	vw B			
2126	~2138	w	2090 w		2164
	{ 1886	s		{ 1905*	2053
1857	{ 1876	s	1870 s	{ 1887	1830
	{ 1848	s		{ 1829*	
1720	1724	m sh			
1602	{ 1619	s	1590 s	{ 1624*	1615
	{ 1579	s		{ 1596	
1380	1301	s	1304 s	{ 1303	1309
1260?		vw		{ 1290*	
~1046	~1057	m B			
{ ~802	{ ~804	m sh			
782	781	s	782 m	{ 788	770
625	625	m		{ 787*	
532	532	vw			
406	407	m			
	320	m			

Key: s - strong, m - medium, w - weak, v - very, B - broad, sh - shoulder.
* - band assigned to the unstable O_2NO_2 molecule.

- (a) Snyder and Hisatzume: (12).
- (b) Pateley, Bent and Crawford: (5).
- (c) D'Or and Tarte: (3).

Such irregular behavior of N_2O_3 spectrum might be interpreted in terms of phase transition of N_2O_3 as reported by Head and Lipscomb (11) or in terms of two different structures, i.e. $\text{ON}-\text{NO}_2$ and OONO as reported by Pateley et al. (5). Although there was striking similarities in the spectrum and good agreement in the frequency values of intense bands between the data of Pateley, Bent and Crawford and the unusual spectra obtained in this work, which would support their proposal, the stability of the two molecular species of N_2O_3 must be investigated further.

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**INFRARED ABSORPTION SPECTRUM OF
SOLID DINITROGEN TRICHLIDE**

by

KEE HYUN RHEE

B. S., Chosun University, Suungju, Korea, 1953

AN ABSTRACT OF A THESIS

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The infrared absorption spectrum of a polycrystalline film of dinitrogen trioxide in the neighborhood of the reported phase transition temperature of -125°C was studied in the region from 5000 cm⁻¹ to 300 cm⁻¹. The study of the spectrum of dinitrogen trioxide in solid phase required a high vacuum system and low temperature apparatus with special handling techniques because this compound was very unstable, chemically reactive at ordinary temperature, and had a low boiling point.

The polycrystalline film of dinitrogen trioxide was obtained by condensing either a reaction mixture of a stoichiometric amount of nitric oxide and oxygen or a gas mixture of nitrogen dioxide with an excess of nitric oxide onto the surface of the cold window in a low temperature solid cell.

Since equilibria existed between nitric oxide, nitrogen dioxide and dinitrogen trioxide and between nitrogen dioxide and dinitrogen tetroxide, the spectra always showed presence of both dinitrogen trioxide and dinitrogen tetroxide. Nineteen absorption bands were identified as dinitrogen trioxide bands by comparing the spectra of dinitrogen trioxide-dinitrogen tetroxide solid mixture with that of pure dinitrogen tetroxide.

The spectra were found to be influenced by several factors such as the concentration ratio of dinitrogen trioxide to dinitrogen tetroxide, the temperature of the cold window during the deposition of the sample, the method of sample condensation, and the subsequent temperature of the sample during runs. A qualitative study of temperature dependence of the spectra showed that dinitrogen trioxide could exist as a stable solid without any dissociation or reaction with the window provided the temp-

erature of the window was below about -110°C . The occurrence of a phase transition was supported by slight differences between two sets of spectra which were taken at about -130°C and -110°C , but the exact transition temperature could not be determined. Furthermore, some spectra supported the existence of two different molecular species of dinitrogen trioxide, i.e. ONNO_2 and OONO_2 , depending upon the experimental conditions.